Implementation of the Optimized Effective Potential Method within Projector Augmented Wave Scheme

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Motivation

1. The optimized effective potential (OEP) or exact exchange (EXX) formalism is a method which can improve the accuracy of DFT because its ability to avoid self-interaction contributions and more generally treat orbital-dependent functionals.

2. The Projector Augmented Wave (PAW) formalism is an efficient pseudopotential-like scheme, which allows for an accurate treatment of the multipole moments in the Hartree and Exchange interactions, making it a natural choice for implementing OEP.

Outline of Talk

1. Explain a OEP Gradient Search Algorithm (R. A. Hyman et al, PRB 62, 15521 (2000)).

2. Explain a Frozen Core + OEP Gradient Search Algorithm that we developed, with focus on:

   Decoupling of valence and core orbital contributions

3. In the end, explain our PAW + OEP Gradient Search algorithm. Show some early results.
Main equations

Starting With Kohn-Sham equation:

\[ \left\{ -\frac{\hbar^2}{2m} \nabla^2 + V_s(r) \right\} \phi_n(r) = \epsilon_n \phi_n(r) \]

where

\[ V_s(r) = V_N(r) + V_H(r) + V_{xc}(r) \]

and the local exchange potential is defined as:

\[ V_{xc}(r) = \frac{\partial E_{xc}[\{\phi_n\}]}{\partial n(r)}. \]

The total energy is given by:

\[ E_{tot}[n] = E_T[n] + E_N[n] + E_H[n] + E_{xc}[\{\phi_n(r)\}]. \]

For the exchange-correlation energy \( E_{xc} \), we use the **exact exchange functional**, and at this moment, we set \( E_c = 0 \)

**Exact Exchange Functional (EXX)**

\[
E_x[\{\phi_n(r)\}] = -\frac{e^2}{2} \sum_{nm} \Theta_n \Theta_m \delta_{\sigma_m \sigma_n} \int d^3r \int d^3r' \phi_n^*(r) \phi_m^*(r') \phi_n(r') \phi_m(r) \frac{1}{|r-r'|}
\]

Because the exact exchange energy is orbital dependent, determining local potential \( V_x(r) = \frac{\partial E_x[\{\phi_k\}]}{\partial n(r)} \) involves solving integral equations. Alternatively, \( V_x(r) \) can be solved by minimizing the energy with constraints, suggested by Hyman, Stiles and Zangwill (PRB 62, 15521 (2000)) and Kümmel Perdew (PRL 90, 043004 (2003))

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Hyman suggested that the OEP object function $F$ to be minimized can be constructed from the total energy and constraint relations.

**All Electron OEP Object Function**

$$F^{AE} = E_{tot}[\{\phi_n\}] - \sum_n \lambda_n (\langle \phi_n | \phi_n \rangle - 1) - \sum_n \langle g_n | H_{ks} - \epsilon_n | \phi_n \rangle$$

1. $\lambda_n$ Lagrangian multiplier $\leftarrow$ Normalization Constraint
2. $g_n(r)$ Lagrangian multiplier function(Auxiliary Function) $\leftarrow$ KS equation Constraint
3. $g_n(r), \lambda_n, \phi_n(r), \epsilon_n, v_x(r)$ independent variables(functions)

For the Frozen Core treatment, only valence orbitals $\phi_v(r)$ are treated variationally, and orbitals associated with core states $\phi_c(r)$ are "frozen" at their reference configuration.

**Frozen Core OEP Object Function**

$$F^{FC} = E_{tot}[\{\phi_v\}] - \sum_v \lambda_v (\langle \phi_v | \phi_v \rangle - 1) - \sum_v \langle g_v | H_{ks} - \epsilon_v | \phi_v \rangle$$

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**Gradient Search Algorithm: All Electron And Frozen Core**

### AE Gradient Search

**AE KS Equation Constraint**

\[
\frac{\partial F}{\partial g_n^*(r)} = 0 \rightarrow (\epsilon_n - H_{KS})\phi_n = 0
\]

**All Electron Shift Function**

\[
s(r) = \frac{\partial F}{\partial V_x} = -\sum_n (g_n^*(r)\phi_n(r) + c.c) \rightarrow \text{Update} V_x
\]

**All Electron Auxiliary Function**

\[
(H_{KS} - \epsilon_n) g_n(r) = \frac{\partial E_x}{\partial \phi_n^*(r)} - V_x\phi_n(r) - U_n\phi_n(r)
\]

**Orthogonalization Constraints**

\[
\frac{\partial F}{\partial \epsilon_n} = 0 \rightarrow \langle g_n | \phi_n \rangle = 0
\]

### FC Gradient Search

**FC KS Equation Constraint**

\[
\frac{\partial F}{\partial g_v^*(r)} = 0 \rightarrow (\epsilon_v - H_{KS})\phi_v = 0
\]

**Frozen core Shift Function**

\[
s(r) = \frac{\partial F}{\partial V_x^{\text{valence}}} = -\sum_v (g_v^*(r)\phi_v(r) + c.c)
\]

**Frozen core Auxiliary Function**

\[
(H_{ks} - \epsilon_v) g_v(r) = \frac{\partial (E_x^{\text{valence}})}{\partial \phi_v^*} - V_x^{\text{valence}}\phi_v(r) - U_v\phi_v(r)
\]

**Orthogonalization Constraints**

\[
\frac{\partial F}{\partial \epsilon_v} = 0 \rightarrow \langle g_v | \phi_v \rangle = 0
\]
How to decouple the differential equation for the auxiliary function:

**AE Auxiliary Function**

\[(H_{KS} - \epsilon_n)g_n(r) = \frac{\partial E_x}{\partial \phi_n^*(r)} - V_x\phi_n(r) - U_n\phi_n(r)\]

**Energy and Orbitals**

\[
\phi_n(r) \rightarrow \phi_c(r), \phi_v(r) \\
E_x \rightarrow E_x^{c-c} + E_x^{v-c} + E_x^{v-v}
\]

**Derivatives**

\[
\frac{\partial E_x}{\partial \phi_n^*(r)} \rightarrow \frac{\partial E_x^{c-c}}{\partial \phi_c^*(r)}, \frac{\partial E_x^{c-v}}{\partial \phi_c^*(r)}, \frac{\partial E_x^{c-v}}{\partial \phi_v^*(r)}, \frac{\partial E_x^{v-v}}{\partial \phi_v^*(r)}
\]

**Auxiliary Function: Core and Valence**

\[(H_{KS} - \epsilon_n)g_n(r) \rightarrow \left\{ \begin{array}{l}
(H_{KS} - \epsilon_c)g_c(r) \\
(H_{KS} - \epsilon_v)g_v(r)
\end{array} \right.\]

**Exchange Potential Partitioning**

\[V_x(r) = V_x^{\text{core}}(r) + V_x^{\text{vale}}(r)\]
Gradient Search Algorithm
All Electron And Frozen Core

How to decouple the differential equation for the auxiliary function:

**AE Auxiliary Function**

\[
(H_{KS} - \varepsilon_n)g_n(r) = \frac{\partial E_x}{\partial \phi_n^*(r)} - V_x \phi_n(r) - U_n \phi_n(r)
\]

**Frozen core Auxiliary Function**

\[
(H_{KS} - \varepsilon_v)g_v(r) = \frac{\partial (E_x^v - v)}{\partial \phi_v^*} - V_x^{vale} \phi_v(r) - U_v \phi_v(r)
\]

**Frozen core Shift Function**

\[
s(r) = \frac{\partial F}{\partial V_x^{vale}} = - \sum_v (g_v^*(r)\phi_v(r) + c.c) \rightarrow Update V_x^{vale}
\]
Motivation and Outline
PAW OEP Formalism and Implementation
Conclusion

All Electron And Frozen core OEP
PAW + OEP

### AE results: Ground State Energy

#### Total ground-state energies for H through Ar (Ry)

<table>
<thead>
<tr>
<th>Atom</th>
<th>Present Work</th>
<th>Previous Work⁽ᵃ⁾</th>
<th>SUHF⁽ᵃ⁾</th>
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#### Total ground-state energies for K through Kr (Ry)

<table>
<thead>
<tr>
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<th>Previous Work⁽ᵃ⁾</th>
<th>SUHF⁽ᵃ⁾</th>
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⁽ᵃ⁾ Grabo, Kreibich, Kurth, & Gross, in Ansimov, ed. *Strong coulomb correlations in electronic structure calculations,* (Gordon and Breach, 2000), pg. 203.
AE results: Exchange potential of 1st and 2nd Row

Exchange potential of C N O F

Exchange potential of Si P S Cl

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AE results: Comparing EXX and LDA of Fluorine

- $rV_x$ Fluorine EXX and LDA result
- Density of Fluorine EXX and LDA result

Graphs showing differences between EXX and LDA for Fluorine at various distances.

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FC results: Partitioning of $V_{x\text{core}}$ and $V_{x\text{valence}}$

**Nitrogen**

\[ N : 1s^2 \underbrace{2s^22p^3}_{\text{core}} \underbrace{2p^3}_{\text{valence}} \]

**Phosphorus**

\[ P : 1s^22s^22p^6 \underbrace{3s^23p^3}_{\text{core}} \underbrace{3s^23p^3}_{\text{valence}} \]
FC results: Partitioning of $V_{x\text{core}}$ and $V_{x\text{val}}$

**Iron**

- $Fe: 1s^12s^22p^63s^23p^6\,3d^64s^2$
  - $rV_x$
  - $rV_{x\text{val}}$
  - $rV_{x\text{core}}$

**Copper**

- $Cu: 1s^12s^22p^63s^23p^6\,3d^94s^2$
  - $Cu:rV_x$
  - $Cu:rV_{x\text{val}}$
  - $Cu:rV_{x\text{core}}$
FC results: Test of FC approximation

Fe: $3d^64s^2 \rightarrow 3d^74s^1$

1. $1s^12s^22p^63s^23p^63d^64s^2$
   - All electron

2. $1s^12s^22p^63s^23p^63d^74s^1$
   - All electron

- $1s^12s^22p^63s^23p^6$ core
- $3d^64s^2$ valence

- $1s^12s^22p^63s^23p^63d^74s^1$
   - $1s^12s^22p^63s^23p^6$ core
   - $3d^74s^1$ valence
FC results: Test of FC approximation

Fe: $3s^2 3p^6 3d^6 4s^2 \rightarrow 3s^2 3p^6 3d^7 4s^1$

1. $1s^1 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$
   - Allelectron

2. $1s^1 2s^2 2p^6 3s^2 3p^6 3d^7 4s^1$
   - core
   - valence

3. $1s^1 2s^2 2p^6 3s^2 3p^6 3d^7 4s^1$
   - core
   - valence

- $1s^1 2s^2 2p^6 3s^2 3p^6 3d^7 4s^1$
- Allelectron

Graph showing $rV_x$ vs. $R(\text{Bohr})$ with curves labeled 'AE' and 'FC[Ne]'.
Atom centered functions needed for PAW calculation

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Meaning</th>
<th>Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\phi_i^a(r)$</td>
<td>AE basis function</td>
<td>AE Kohn-Sham eigenstate</td>
</tr>
<tr>
<td>$\tilde{\phi}_i^a(r)$</td>
<td>PS basis function</td>
<td>Constructed; $\tilde{\phi}_i^a(r) \equiv \phi_i^a(r)$ for $r \geq r_c^a$</td>
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<tr>
<td>$p_i^a(r)$</td>
<td>Projector function</td>
<td>$p_i^a(r) \equiv 0$ for $r \geq r_c^a$ and $\langle p_i^a</td>
</tr>
</tbody>
</table>

PAW transformation from PS $\tilde{\Psi}_n(r) \rightarrow$ AE $\Psi_n(r)$

$$\Psi_n(r) = \tilde{\Psi}_n(r) + \sum_{ai} \left( \phi_i^a(r) - \tilde{\phi}_i^a(r) \right) \langle p_i^a | \tilde{\Psi}_n \rangle$$

- Corrections
- $a$: site index
- $i$: basis index
Kohn-Sham equations in PAW formalism

\[(H^{PAW} - \varepsilon_n O)\tilde{\psi}_n(r) = 0\]

PAW Hamiltonian

\[H^{PAW}(r) = \tilde{H}(r) + \sum_{aij} |p_i^a\rangle D_{ij}^a \langle p_j^a|\]

Smooth Hamiltonian and Smooth Effective Potential

\[\tilde{H} = -\frac{\hbar^2}{2m} \nabla^2 + \tilde{V}\]

\[\tilde{V}(r) = \tilde{V}_{loc}(r) + \tilde{V}_{H}(r) + \tilde{V}_{val}(r)\]

\(\tilde{V}_{loc}\) is unscreened local potential

PAW Matrix Elements

\[D_{ij}^a = \langle \phi_i^a | H | \phi_j^a \rangle - \langle \tilde{\phi}_i^a | \tilde{H} | \tilde{\phi}_j^a \rangle\]

Contains All electron part, and corrections

PAW Overlap Function

\[O = 1 + \sum_{aij} |p_i^a\rangle O_{ij}^a \langle p_j^a|\]

\[O_{ij}^a \equiv \langle \phi_i^a | \phi_j^a \rangle - \langle \tilde{\phi}_i^a | \tilde{\phi}_j^a \rangle\]
**PAW + OEP Formalism**

### All Electron OEP Object Function

\[
F^{AE} = E_{tot}[\{\phi_n\}] - \sum_n \lambda_n (\langle \phi_n | \phi_n \rangle - 1) - \sum_n \langle g_n | H_{ks} - \varepsilon_n | \phi_n \rangle
\]

### Frozen Core OEP Object Function

\[
F^{FC} = E_{tot}[\{\phi_v\}] - \sum_v \lambda_v (\langle \phi_v | \phi_v \rangle - 1) - \sum_v \langle g_v | H_{ks} - \varepsilon_v | \phi_v \rangle
\]

The PAW Object Function can be constructed in the same way, with similar constraints:

### PAW OEP Object Function

\[
F^{PAW} = E_{tot} - \sum_v \lambda_v (\langle \tilde{\psi}_v | O | \tilde{\psi}_v \rangle - 1) - \sum_v \langle \tilde{g}_v | H_{PAW}^{OEP} - \varepsilon_v O | \tilde{\psi}_v \rangle
\]
**Motivation and Outline**

**PAW OEP Formalism and Implementation**

**Conclusion**

**All Electron And Frozen core OEP**

**PAW + OEP**

---

**PAW Gradient Search Algorithm**

**Frozen Core And PAW**

### FC Gradient Search

**Frozen core Shift Function**

\[
\frac{\partial F}{\partial V_{\text{valex}}} = - \sum_v (g_v^*(r) \phi_v(r) + c.c)
\]

**Frozen core Auxiliary Function**

\[
(H_{ks} - \epsilon_v)g_v(r) = \frac{\partial (E_X^{\text{v-v}})}{\partial \phi_n^*} - \nu_{\text{valex}} v(r) \phi(r) - U_v \phi_v(r)
\]

---

### PAW Gradient Search

**PAW OEP Shift Function**

\[
S(r) = \frac{\partial F_{\text{PAW}}}{\partial V_{\text{valex}}} = - \sum_v (g_v^*(r) \tilde{\psi}_v(r) + c.c)
\]

\[
[S]_{ij} = \frac{\partial F_{\text{PAW}}}{\partial [V_{\text{valex}}]_{ij}} = - \sum_v \langle \tilde{g}_v | p_i \rangle \langle p_j | \tilde{\psi}_v \rangle + c.c.
\]

**PAW Auxiliary Function**

\[
(H_{\text{PAW}} - E_v O)g_v = \frac{\partial E_X^{\text{v-v}}}{\partial \psi_v^*} - \nu_{\text{valex}} \tilde{\psi}_v - U_v \tilde{\psi}_v
\]

\[
- \sum_{ij} |p_i \rangle \langle V_{\text{valex}} v_{ij} | p_j \rangle \tilde{\psi}_v
\]
Construction of $\tilde{V}_{loc}$

$\tilde{V}_{loc}$ is a short range unscreened local potential related to the reference pseudopotential $V^{ps}(r)$ according to:

$$\tilde{V}_{loc}(r) = V^{PS}(r) - V_{H}[\tilde{\rho}_v] - \tilde{V}^{v_{ale}}(r)$$
Atompaw OEP results: PAW pseudized exchange potential

\[ \tilde{V}_x \] of N

\[ \tilde{V}_x \] of P

\[ \tilde{V}_x = \tilde{V}_{x,\text{paw}} + \tilde{V}_{x,\text{vale}} \]
Implement a gradient search algorithm → All Electron + OEP code.
Developed a Frozen core scheme; decouple the equations for core and valence contributions.
We examined some elements, and showed that we can improve the FC accuracy by including more orbitals in the valence.
Developed PAW + OEP scheme, constructed the \( \tilde{\phi}_n(r), p_i(r), D_{ij}, \tilde{V}_{loc} \)
Future work: PAW + OEP solid code